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**ACIDITY DEPENDENCE ON CLOUD DROP SIZES, ENHANCEMENT OF
SULFATE PRODUCTION IN CLOUDS AND ITS CLIMATIC
IMPLICATIONS FROM CLOUD WATER COLLECTED AT A REMOTE
EASTERN U.S. SITE**

by
BRYAN DOUGLAS LOGIE

A thesis submitted to the Graduate Faculty of
North Carolina State University
in partial fulfillment of
the requirements for the Degree of
Master of Science

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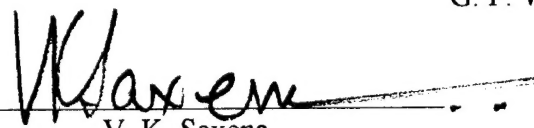
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Field Intercomparisons of a Passive and Active Cloud Water Collector From Data
Collected at a Remote Eastern U.S. Site*

by

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ABSTRACT

Two different cloud water collectors were operated simultaneously on a mountain-top platform in Mt. Mitchell State Park, North Carolina ($35^{\circ} 44' 05''$ N $82^{\circ} 17' 15''$ W) to assess differences, if any, in measured acidity, ionic concentrations, and liquid water collection efficiencies during the summer, 1994. The cloud water collectors used were the Daube California Institute of Technology active-string collector (CALTECH) and the non-rotating passive Atmospheric Sciences Research Center string collector. Both collectors transfer cloud water into their sampling bottles by a process analogous to the collision-coalescence process in precipitation initiation by which cloud droplets accumulate on the collector strings and are then transferred to collection bottles as the droplets become large enough to fall. These large drops, in turn, acquire smaller droplets along their path. The tests, covering a one month period consisting of 22 cloud events, showed cloud water acidity measurements, made within minutes of sample collection at the site, frequently differed outside the error limits of the pH measurement device between the two collectors. This was found to be a consequence of sampling with the precipitation shield attached to the CALTECH collector causing a small droplet sampling bias for the instrument. Cloud water samples taken during events where the average droplet size was large showed larger differences in pH between the two collectors than events where the average droplet was smaller.

*Presented at the Ninth Symposium on Meteorological Observations and Instrumentation, Charlotte, North Carolina, March 27-31, 1995.

ABSTRACT

LOGIE, BRYAN DOUGLAS. Acidity Dependence on Cloud Drop Sizes, Predicted Enhancement in Sulfate Production in Clouds and its Climatic Implications from Cloud Water Collected at a Remote Eastern U.S. Site. (Under the direction of Vinod K. Saxena.)

SECTION I. Two different cloud water collectors were operated simultaneously on a mountain-top platform in Mt. Mitchell State Park, North Carolina ($35^{\circ} 44' 05''$ N $82^{\circ} 17' 15''$ W) to assess differences, if any, in measured acidity, ionic concentrations, and liquid water collection efficiencies during the summer, 1994. The cloud water collectors used were the Daube California Institute of Technology active-string collector (CALTECH) and the non-rotating passive Atmospheric Sciences Research Center string collector. Both collectors transfer cloud water into their sampling bottles by a process analogous to the collision-coalescence process in precipitation initiation by which cloud droplets accumulate on the collector strings and are then transferred to collection bottles as the droplets become large enough to fall. These large drops, in turn, acquire smaller droplets along their path. The tests, covering a one month period consisting of 22 cloud events, showed cloud water acidity measurements, made within minutes of sample collection at the site, frequently differed outside the error limits of the pH measurement device between the two collectors. This was found to be a consequence of sampling with the precipitation shield attached to the CALTECH collector causing a small droplet sampling bias for the instrument. Cloud water samples taken during events where the average droplet size was large showed

larger differences in pH between the two collectors than events where the average droplet was smaller.

SECTION II. Acidity variations between cloud droplets of different sizes are predicted in models, however, measurements made in natural clouds to verify this are extremely limited. The heterogeneity in cloud droplets may lead to increased sulfate production in clouds exceeding calculations made using bulk cloud water characteristics. During the spring, 1995, a size-fractionating version of the California Institute of Technology active strand cloud water collector was operated on a mountain-top platform in Mt. Mitchell State Park, North Carolina ($35^{\circ} 44' 05''$ N $82^{\circ} 17' 15''$ W) to determine, experimentally, whether acidity variations between large and small cloud droplets are common in nature as models suggest. Differences of up to 0.6 pH units were common for the sampled clouds with the small cloud droplets generally more acidic than the large droplets. We did collect several samples, however, where the large cloud droplets were more acidic. This chemical heterogeneity, though seemingly small, can significantly enhance oxidation of sulfur dioxide to sulfate within clouds, relative to oxidation rates predicted using bulk water samples. Our findings indicate that sulfate production rates, which could enhance cloud condensation nuclei, are underestimated by at least 5%, compared to bulk water calculations, for over 30% of our samples. These results suggest that sulfate production within clouds may be more rapid than previously theorized. In this paper we not only examined cloud droplet chemical inhomogeneity between droplet sizes, but also examined the effect of air mass origin on those variations.

DEDICATION

It was only through the efforts of several people that this work was possible. To the Cloud Physics group at North Carolina State University I extend my gratitude for working around the clock to gather data at Mt. Mitchell, their encouragement, and especially their patience. Thank you.

While it is true that this paper is a result of a team effort, I give my greatest thanks to my wife Colleen and sons Nicholas and Matthew. Though I was the one buried in my computer til all hours, and it was I who spent many weeks away gathering data, they gave up the most so that I might shine by putting up with me as I struggled to write a paper or work a problem. To Colleen, thank you for taking care of the little ones so I could work in peace. To Nicholas and Matthew, though you may have forgotten by the time you are old enough to read this, I'm sorry I couldn't spend as much time with you as you would have liked, but hopefully your sacrifice will have made me a better person. Without all of your help, I wouldn't have made it this far. I love you all.

BIOGRAPHY

Bryan Logie was born in Castro Valley, California, on 17 March 1959. He was raised in Capitola, California, where he attended Soquel High School. Following graduation, he enlisted in the Air Force and entered active duty on 1 July 1977. After completing Basic Military Training at Lackland Air Force Base, Texas, he received training as a Weather Specialist at Chanute Air Force Base, Illinois.

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In 1993 the Air Force Institute of Technology selected Bryan to attend graduate school at North Carolina State University.

Bryan was married to the former Colleen Maynard on June 17, 1982. They have two sons, Nicholas and Matthew.

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The contents of this thesis do not necessarily reflect either the views of the U.S. Air Force or the U.S. Department of Energy.

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Field Intercomparisons of a Passive and Active Cloud Water Collector From Data
Collected at a Remote Eastern U.S. Site

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1. INTRODUCTION

Cloud water chemistry is important because of its potential effect on the environment. Additionally, cloud water provides a unique opportunity for investigating the origin of air masses since it represents the end product of natural processes enabling us to detect very low concentrations of water soluble species in the air. A knowledge of the temporal variation in ions and acidity in clouds is important in determining the potential acidic deposition due to the direct cloud capture mechanism (Saxena and Lin, 1990). It is through collection of cloud water these processes are investigated.

Several studies have shown that no two cloud water collectors yield the same chemical composition (e.g. McLaren et al., 1985; Hering et al., 1987; Collett et al., 1989; Mohnen and Kadlec, 1989; DeFelice and Saxena, 1990), with differences attributed to different methods of operation, or within the error limits of the measurement devices. During the summer 1994, two cloud water collectors were operated simultaneously at a field station on Mt. Gibbs (elev. 2006 m) in Mt. Mitchell (35° 44' 05" N 82° 17' 15" W - the highest peak in the eastern U.S) State Park, North Carolina. The collectors used were an Atmospheric Science Research Center (ASRC), Albany, New York passive cloud water collector (Castillo et al., 1983; Saxena et al., 1989; DeFelice and Saxena, 1990) and a Daube California Institute of Technology active-string collector (CALTECH) (Daube et al., 1987) mounted together on a carriage at the top of an observation tower (Fig 1.) above the forest canopy which often stayed immersed in clouds. Passive collectors depend upon ambient wind speed to provide the velocity differential between suspended cloud droplets and the collector surface, while active collectors provide some physical means (such as a fan in the CALTECH collector) for generating the velocity difference thus drawing the sample to the device.

During the course of our experiment, we discovered the observed pH frequently differed between the ASRC and the CALTECH collected cloud water for the same cloud, and same collection period, and these variations were frequently outside the error limits of the pH measuring device. Additionally, ionic concentrations of Cl, Na,

K, Ca and Mg frequently differed by more than 20 percent (sometimes much higher) between samples collected by the two instruments. While others have compared the operation of these same two collectors (Mohnen and Kadlecek, 1989; DeFelice and Saxena, 1990), they did not encounter significant pH differences in their experiments, nor did they examine more than a few ionic concentrations when comparing cloud water collected by the two devices. It is also unclear from the previous studies whether cloud water collections made with the CALTECH collector were made with the precipitation shield attached for all cloud events, or only during rainfall.

The variations in cloud water pH are significant between the two devices since sulfur oxidation rates in clouds are often predicted based on average, or bulk, cloud water properties. As shown by Saxena and Grovenstein (1994), Saxena et al. (1995) and Burns et al. (1995), higher concentrations of sulfates in clouds results from increased numbers of cloud condensation nuclei (CCN). This increase in CCN in turn increases the cloud droplet number concentration leading to increased cloud albedo. This increase in cloud albedo is thought to be enough to counter the effect of greenhouse warming caused by anticipated increases in CO₂ levels in the atmosphere (Ghan et al., 1990; Leitch et al., 1992). If the CALTECH cloud water collector, with the rain hood attached, has a sampling bias toward smaller cloud droplets, calculations of sulfur oxidation rates previously made using data from this device may be in error. This in turn may also partially invalidate previous conclusions made about cloud chemical compositions, especially in cases where the CALTECH was the only cloud water collecting instrument (e.g. Collett et al., 1989).

The CALTECH collector can also be used to determine cloud liquid water content (LWC). Collett et al. (1989) used theoretical collection efficiency to determine LWC, however, we have determined an empirical equation for LWC calculation based on collected cloud water mass and have compared our results to LWC values derived from a gravimetric device, integration of Forward Scattering Spectrometer data and as determined from an empirical relationship based on collected water mass using a passive cloud water collector. This is useful in that, aside from a 12 volt battery used to power the CALTECH fan, no other equipment is needed to collect cloud water and

determine LWC. This makes the collector ideal for remote stations with no easy access to electricity, and can be used under both rain-free and precipitation cloud events.

The purpose of this paper is twofold; to attempt to identify the cause(s) for the pH and chemical differences observed during our experiment between the ASRC and CALTECH cloud water collectors, and to demonstrate how the CALTECH collector can be used to determine cloud liquid water content.

2. EXPERIMENTAL SITE AND INSTRUMENTATION

The experimental site for this study is located at Mt. Gibbs (2006 m MSL), approximately 2 km south of Mt. Mitchell, North Carolina. The site is ideal for *in situ* cloud measurements as the area is immersed in clouds nearly 70% of the time during the summer (Saxena et al., 1989, 1994), while being influenced by varying air mass types; highly polluted air from the Ohio Valley region, clean maritime air and relatively clean continental air from the great plains (Saxena and Yeh, 1988). Additionally, there is no local source of pollution near the experiment site.

The period of observations for this experiment ran from mid July 1994 for four weeks covering 22 cloud events and 127 cloud samples (82 of which were from non-precipitating clouds). Cloud water pH varied from a low of 3.02 to a high of 5.27. An observation tower, 16.5 m tall extending 10 m above the forest canopy, was fully instrumented with meteorological sensors for wind speed and direction, ambient temperature, relative humidity, barometric pressure and solar radiation. The cloud water collectors used in this experiment were manually operated on an hourly basis upon the occurrence of a cloud event. A cloud event began when visibility was reduced to less than 1 km for a period of at least 15 minutes. The cloud water collected was tested for pH within 10 minutes of collection using two samples, if sufficient quantity had been collected, with the remainder refrigerated at 4°C for later chemical analysis. Additionally, for the majority of the cloud events, the final cloud water sample was followed by a control sample of deionized water to help validate lab analysis results. The chemical composition of the collected cloud water was analyzed with conventional USA EPA QA/QC procedures by the Soil Sciences Lab operating at North Carolina State University. The liquid water content of the clouds (LWC) was determined using a Forward Scattering Spectrometer Probe (FSSP) (Dye and Baumgardner, 1984), an RPM sampler, designed by the Tennessee Valley Authority (TVA) (Valente et al., 1989; Arends et al., 1992), and by an empirical relationship between collected cloud water mass and LWC derived for the ASRC (Saxena et al., 1989; DeFelice and Saxena, 1990).

.. ..

Air mass trajectories for all cloud events were calculated using the Hybrid Single-Particle Lagrangian Integrated Trajectories (HY-SPLIT) Model (Version 3.0) developed at the National Oceanic and Atmospheric Administration (Draxler, 1992) to determine whether there was a correlation between the originating air mass for a particular cloud and measured pH differences for the event. Three sectors, identified as the polluted sector, from 290° to 65° azimuth relative to the site, the continental sector, 240° to 290° azimuth, and the marine sector, 65° to 240° azimuth, were used to classify the cloud forming air masses.

3. RESULTS AND DISCUSSION

a) Teflon String Collectors

Both the CALTECH and ASRC utilize the same basic mechanism for transferring cloud water to their respective collection bottles. As shown by DeFelice and Saxena (1990), the devices do have mechanical differences affecting their collection efficiencies, hence the amount of cloud water collected by each. These differences are shown in Table 1. Our assumption is that the temporal and spacial variation in the clouds sampled are small. Because sampling periods averaged approximately one hour between sample collections, it was necessary to identify situations likely to exhibit minimum variability in cloud composition over the sampling period (Schwartz et al., 1982).

The CALTECH collector was operated with the rain shield (Daube et al., 1987) attached for all observations. While this simplified operations, it may have also contributed to the pH differences in many of the collected samples. Since the inlet to the CALTECH is 90 degrees from the wind flow, we essentially have an anisokinetic sampler as described by Hinds (1982). In anisokinetic sampling, particles with high inertia in the volume of air sampled will be unable to make the turn quickly enough to enter the collector inlet, and will not be included in the sample. This suggests that larger cloud droplets, in addition to rain drops, will be excluded from the cloud water sample. The rain shield was tested by Daube et al. (1987) by pouring water over the inlet and visually determining whether the simulated rain water was drawn into the sampler. This procedure showed the rain hood effectively excluded rain water from the sample, however, the effect the rain hood would have on larger cloud droplets was not considered.

b) pH Trends

It is important to emphasize that the results reported in this study are based on mountain-top field tests and not idealized laboratory tests. To investigate the differences in pH between the two collectors we considered the following possible

causes: 1) dependence of collection efficiency upon wind speed causing variations in pH, 2) variations due to air mass origin affecting droplet size distributions and acidity, and 3) collector operation.

At present we assume the inclusion of the rain shield on the CALTECH apparatus undersamples the larger cloud droplets due to anisokinetic sampling, in addition to excluding liquid precipitation. Considering smaller droplets are generally more acidic than large (e.g. Hinds, 1982; Collett et al., 1994), the CALTECH cloud water collector should routinely produce samples with lower pH values than either the ASRC or, by extension, the CALTECH collector without the rain hood. This conclusion is generally confirmed by our field measurements, however, in some cases the CALTECH collected cloud water had a pH higher than that collected by the ASRC. This is possibly due to occasions where larger droplets were more acidic than the smaller droplets as has been shown both theoretically by Seidl (1989), Twohy et al. (1989), Hegg and Larson (1990), to name a few, and experimentally by Munger et al. (1989) and Collett et al. (1994). As a visual inspection of Fig. 2 indicates, the average of all our measurements for each air mass does concur with this hypothesis, and the pH differences generally vary from no difference between instruments to lower pH values for the CALTECH. Some of the measurements, however, contained water with a higher pH for samples collected with the CALTECH. We need to examine what could cause the pH difference between the two devices. We will consider whether the pH differences are a result of ambient wind speeds, or is the difference inherent in the operation of the device?

One explanation for the pH variation between devices may be due to the effect that increased wind speeds had on the larger cloud droplets. As previously stated, since we are sampling anisokinetically with the CALTECH, we suspect higher wind speeds would tend to increase the undersampling of the larger droplets due to simultaneous increases in droplet inertia. Since smaller droplets are generally more acidic, the variation in pH between devices should decrease with decreasing wind speed. As shown in Fig. 3, however, we found no correlation between variations in pH values measured by both collectors and wind speed ($R^2 = 0.04$) for the non-

precipitation cases, so the ambient wind is not a factor. Another explanation is needed for the pH variations.

To further investigate differences between the CALTECH and ASRC we looked at nine ions for sample comparison: H^+ , NH_4^+ , Cl^- , NO_3^- , SO_4^{2-} , Na^+ , K^+ , Ca^{2+} and Mg^{2+} . Mohnen and Kadlec (1989) compared only H^+ , NH_4^+ , NO_3^- and SO_4^{2-} when they investigated differences between these two devices. They found approximately 90% of the ratios between the ion concentrations measured by the two instruments (ASRC/CALTECH) were between 0.9 and 1.1 for all ions tested. It is unclear from their research, however, whether they used the rain shield on the CALTECH during non-precipitation events. In contrast, our comparisons of H^+ concentrations, for example, show that in only 43% of the samples collected ratios were between 0.9 and 1.1, while 75% of the samples were between 0.8 and 1.2, 85% between 0.7 and 1.4. The worst agreement in H^+ was for a sample where the CALTECH pH was lower than that from the ASRC by half a pH unit. In contrast to Mohnen and Kadlec's (1989) results, we did not find good agreement between the same ions measured by the two instruments, except when all samples were averaged together. In addition to H^+ , which we already examined, for NH_4^+ , Cl^- , NO_3^- , SO_4^{2-} , Na^+ , K^+ , Ca^{2+} and Mg^{2+} we found only 63%, 31%, 66%, 61%, 20%, 16%, 11% and 8%, respectively, of the ratios between the concentrations measured by the two devices fell within 0.9 and 1.1. Additionally for Na^+ , K^+ , Ca^{2+} and Mg^{2+} less than half the sample concentrations fell between 0.7 and 1.4. It should be noted, however, the concentrations of K^+ , Ca^{2+} and Mg^{2+} were extremely small and any measurement error would greatly magnify differences between the samples collected by the two devices. Additional data on comparison ion concentrations measured by the two devices can be found in Table 2.

In addition to simple chemical comparisons for all cases, we also examined how chemical concentrations varied with the trajectory of the air which produced a particular cloud event to determine whether a particular property associated with air mass origin could account for the discrepancy in observed pH. When broken down by

the air mass origin determined from backward trajectories, we discovered increased differences in most ions, particularly H^+ , for both the continental and marine cases. Both continental and marine air masses have been found to produce larger cloud droplets than the polluted air masses intercepted by Mt. Mitchell (Saxena and Lin, 1990; DeFelice and Saxena, 1991). To determine whether there was a correlation between air mass origin and pH differences between devices, we compared air mass origin and droplet chemistry differences between the two devices for all cloud water collections. For example, in Fig. 4 we compared two events both formed from continental air masses where there was a pH difference between samples (22 Jul 94), and one where there was none (26 Jul 94). We found that for both cases the contribution by the majority of the chemical species were relatively small, however, there were differences of nearly 100% in SO_4^{2-} concentrations between the two sample days. The difference in ion concentrations measured by the two devices were comparatively smaller. Expanding our investigation, we also found significant differences in SO_4^{2-} for the majority of continental cases. For the continental air mass clouds, only 51% of the ratios of the concentrations between the devices fell between 0.9 and 1.1. We then examined droplet size distributions to determine if there was a relationship to the observed pH differences. We discovered that in cases where the pH varied between devices the greatest pH differences occurred where the droplet size distribution was typically broader and consisted of more large droplets (Fig 5). Additionally, in cases where the pH was within measurement error limits (no significant difference) the droplet size distribution was narrower and consisted of generally smaller droplets, such as the case of 26 Jul 94 (Fig 6). This supports the theory that smaller, more acidic cloud droplets are preferentially collected over the larger droplets. By extension, the smaller size droplets found in polluted air (Alkezweeny et al., 1993; Saxena et al., 1994) would tend to have less sampling bias than either maritime or continental air with a larger average drop size.

c) Cloud liquid water content.

An advantage of using either the CALTECH or ASRC cloud water collector to determine cloud liquid water content (LWC) is that both devices are portable and have no special power requirements, other than a 12 volt battery to power the CALTECH fan. Saxena et al. (1989) and DeFelice and Saxena (1990) showed how the ASRC could be used to calculate LWC based on collected cloud water mass. During the 1994 Mt. Mitchell field experiment we compared ASRC collected cloud water mass with LWC measured using an FSSP and a TVA RPM sampler in order to validate earlier results. We analyzed the correlation between the collected water mass from the ASRC and the CALTECH, and found they were very strongly correlated ($R^2 = 0.88$).

We used both the FSSP and TVA samplers to determine representative cloud liquid water content. The LWC can be calculated using the FSSP by:

$$LWC = \frac{\pi}{6} \rho \sum_{i=1}^{15} N_i D_i^3 \quad (1)$$

where ρ is the density of water, N is the droplet count for a particular droplet diameter D . The LWC from the TVA sampler is determined by:

$$LWC = \frac{w}{5.182 \left(\frac{T}{0.2953p} \right)^{1/2} m^{0.48} t} \quad (2)$$

Where w is the weight gain of the filter pack during the sampling period, T is the temperature (C), p is the pressure in millibars, m is the magnehelic setting for the device (determined by wind speed) and t is the sample time in minutes. We found the LWC derived using the FSSP (eq. 1) and that determined by the TVA (eq. 2) were highly correlated ($R^2 = 0.87$), thus increasing our confidence in using either the FSSP or TVA as ground truth LWC values, though Arends et al. (1992) suggests that the TVA sampler is the better device for determining LWC. Since we did not have FSSP data available for all cloud events we chose to use the TVA exclusively for consistency.

Based on cloud water samples, the LWC of clouds for the CALTECH cloud water collector is empirically related to the mass (V in grams) of the collected cloud water during the period (t in minutes) of collection:

$$LWC = 0.12 \text{ min} \cdot \text{m}^{-3} \frac{V}{t} + 0.01 \text{ gm}^{-3} \quad (3)$$

where LWC = Liquid water content in g m^{-3} . The LWC calculated using the CALTECH collected water mass was found to be well correlated ($R^2 = 0.79$) to TVA derived values. The ASRC had a slightly weaker, but significant, correlation ($R^2 = 0.70$), so the CALTECH is as good as the ASRC for evaluating cloud LWC. The CALTECH has two advantages in determining LWC over using the ASRC cloud water relationship, however: first there is little or no rain contamination when using the CALTECH with the rain shield attached, and second there is no lower limiting wind speed for effective collection as when using the ASRC (DeFelice and Saxena, 1990). Further, the CALTECH does not require calibration or meteorological data, such as the FSSP or the TVA RPM sampler. The ASRC, however, does not require a power source, nor does it need to be monitored to ensure it is faces into the wind during sampling.

The empirically derived eq. (3) does not include a term for the face velocity of the airflow on the collecting strands in the instrument. Therefore, this equation must be modified for instruments with internal sampling flows different than that for this experiment. For this instrument the internal sampling flow was 5.6 m s^{-1} . Additionally, eq. (3) was developed for the CALTECH with the rain hood attached. Due to the CALTECH sampling bias for small droplets this equation may not be applicable to a device without the rain hood installed.

4. CONCLUSIONS

With the rain hood attached to the CALTECH cloud water collector, the collected water samples do not always represent the properties of the sampled cloud. The cloud water chemistry was compared for samples taken using the ASRC and CALTECH cloud water collectors in Mt. Mitchell State Park, North Carolina during July and August 1994. Measurements of pH, along with comparisons of several ionic concentrations were markedly different for many of the cloud water samples. The difference between the two collecting devices was found to be unrelated to ambient wind speed, and only varied somewhat with the air mass origin (either continental, marine or a combination of the two). As the CALTECH collector samples anisokinetically (Hinds, 1982) with the rain shield installed, preferential sampling of smaller cloud droplets occurs. Since it is generally accepted that smaller droplets are more acidic than the larger droplets, due to higher concentrations of soluble material in the smaller droplets, generally lower values of pH were found in the CALTECH cloud water. These findings suggest that previous conclusions made about cloud water acidity using the CALTECH may be erroneous if the samples were taken with the rain hood attached and the large and small droplets were chemically heterogeneous. Furthermore, sampling with the rain hood during precipitation will not only exclude rain droplets from entering the sampler, but will also exclude a portion of the larger cloud droplets. This device should be tested under a controlled laboratory environment to determine which droplet sizes are not being representatively sampled.

A relationship was found between collected water mass from the CALTECH and ASRC leading to an empirical equation for determining LWC from cloud water collected from the CALTECH. A gravimetric device was used as ground truth for cloud LWC and ASRC and CALTECH calculated values were tested against it and showed very good correlation. The ASRC has been used previously to determine cloud LWC using an empirical relationship relating LWC to collected cloud water mass, and the CALTECH produces similarly good results. The equation does not take into account internal sampling flow for the CALTECH, however, so any change in

internal flow from our experiment would make the equation invalid, though similar empirical equations can be found in other situations.

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Table 1. Difference between California Institute of Technology active string collector (CALTECH) and Atmospheric Science Research Center non-rotating passive string collector (ASRC) (after DeFelice and Saxena, 1990).

Item	CALTECH	ASRC
String orientation	~ 45° to horizontal	90° to horizontal
String diameter	0.51mm	0.44mm
Effective sample volume	~ 60v*	v*
Mode of operation	Active	Passive
Wind dependence	Must be pointed into the wind	No wind dependence
Operations	Cloud only	Cloud and precipitation collection

*Based on collector measurements

Table 2. Comparison of ionic concentrations between the California Institute of Technology active string collector (CALTECH) and Atmospheric Science Research Center non-rotating passive string collector (ASRC) for non-precipitation cloud events. Data represent the ratio of ASRC measured ion concentrations to the CALTECH (ASRC/CALTECH). Maximum difference determined as a percentage difference between the two collectors (ASRC-CALTECH)/CALTECH.

Ion	Maximum Difference	0.9 to 1.1	0.7 to 1.4
H^+	56%	43%	85%
NH_4^+	105%	63%	88%
Cl^-	235%	31%	68%
NO_3^-	217%	66%	90%
SO_4^{2-}	70%	61%	88%
Na^+	3100%	20%	46%
K^+	1200%	16%	30%
Ca^{2+}	3300%	11%	37%
Mg^{2+}	600%	8%	52%

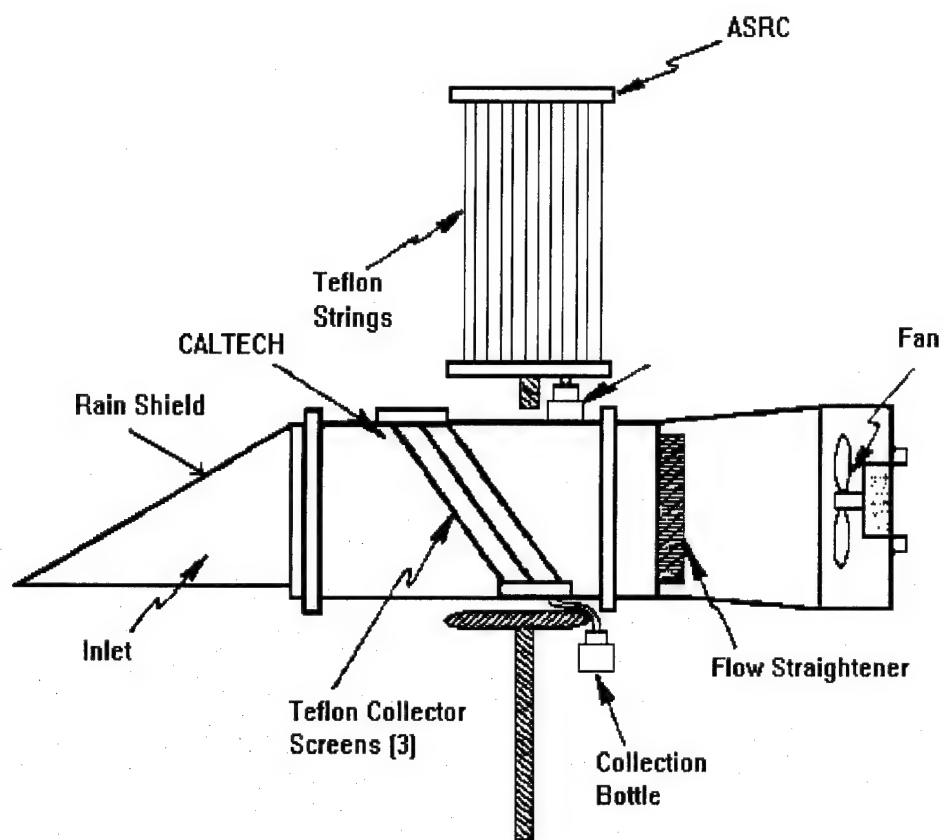


Figure 1. Atmospheric Science Research Center passive string collector (ASRC) and California Institute of Technology active-string collector (CALTECH).

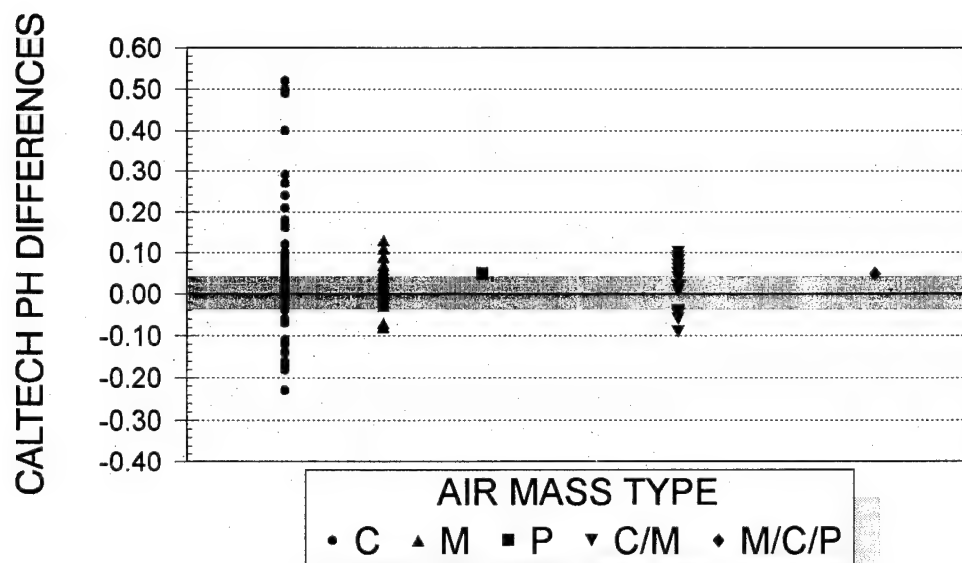


Figure 2. Differences in pH units between the ASRC and CALTECH cloud water collectors by air mass origin. C = continental air, M = marine, P = polluted. Where air mass trajectories crossed defining boundaries, the type is listed as to the domains intersected by the trajectory. Above the zero line indicates the CALTECH collected cloud water had a lower pH for the same ASRC sample. The gray shaded area represents differences within the error limits of the pH measuring instrument. Samples for non-precipitation cases only are considered.

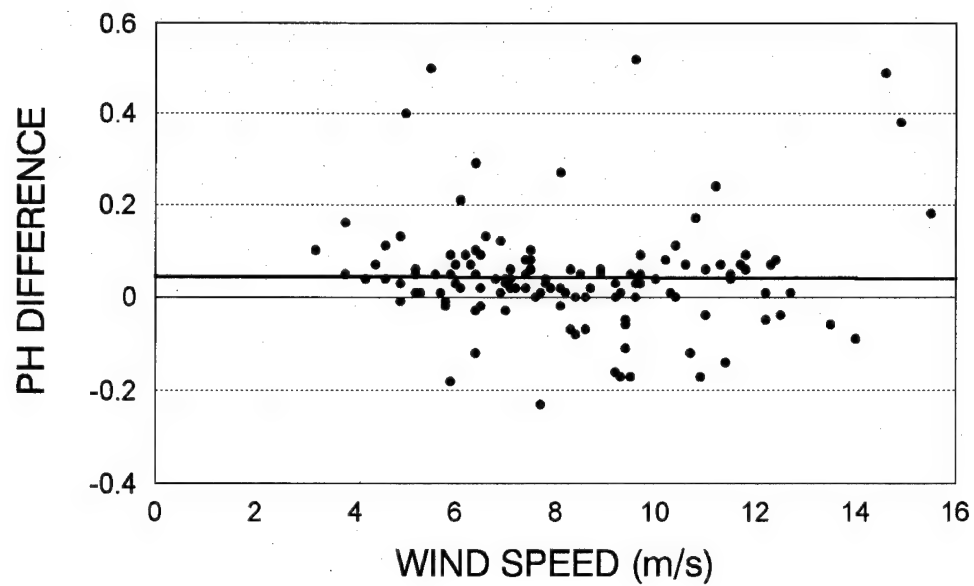


Figure 3. Correlation between differences in pH between the CALTECH and ASRC cloud water collectors and wind speed. Positive differences are for cases where CALTECH pH was lower than that measured from the ASRC. Samples compared for non-precipitation events only.

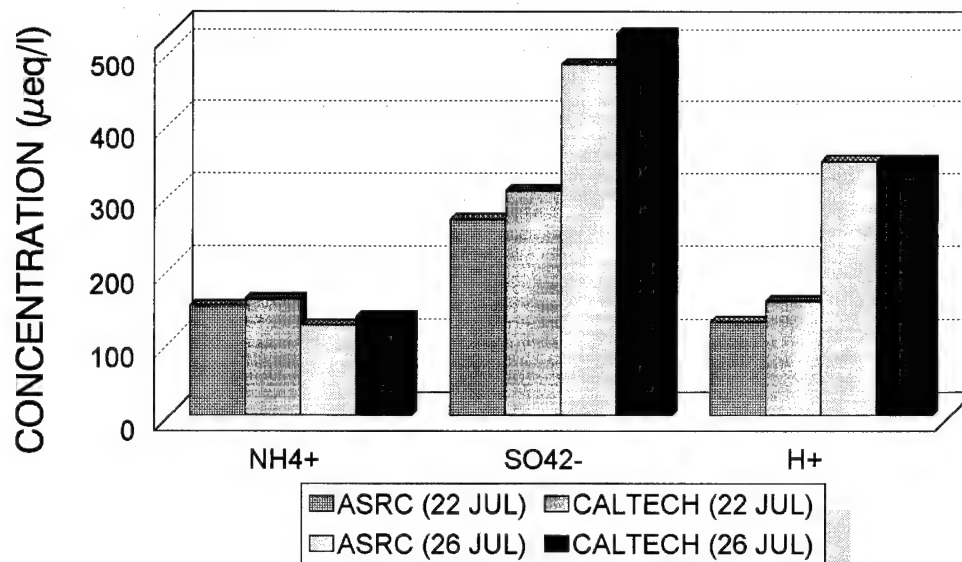


Figure 4. Difference in ionic composition of samples between 26 Jul 94 cloud sample where there was no pH difference between devices and 22 Jul 94 where the CALTECH cloud water pH was 0.1 pH units more acidic. Chemical variations between the samples for Cl^- , NO_3^- , Na^+ , K^+ , Ca^{2+} and Mg^{2+} were also significant, however, the ions depicted are most responsible for sample acidity. Both samples were from clouds formed with a continental air mass origin.

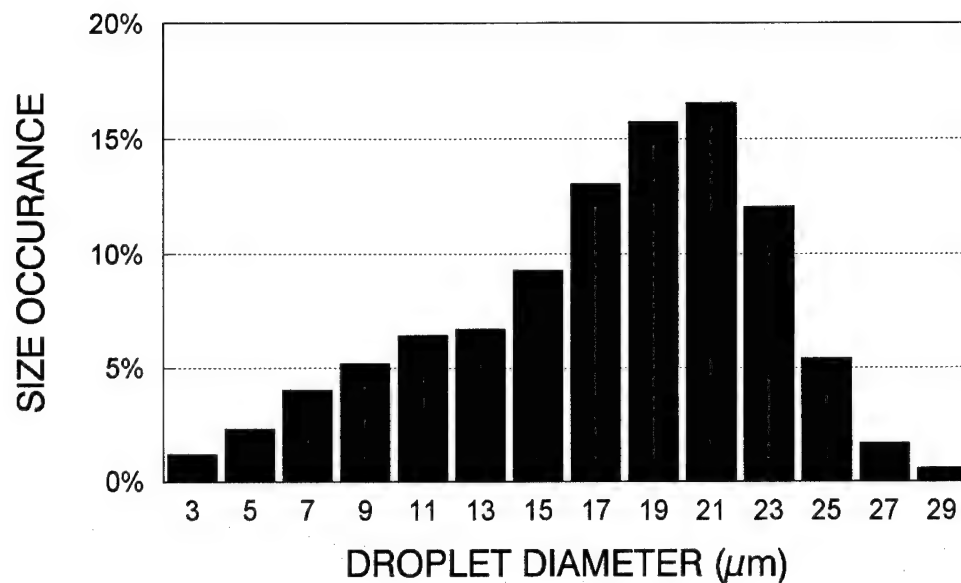


Figure 5. Example of typical droplet distribution where CALTECH and ASRC pH vary outside pH measurement error limits. This case represents a CALTECH pH 0.1 lower than ASRC. Data averaged for 21 Jul 94, 0501-0601 UTC.

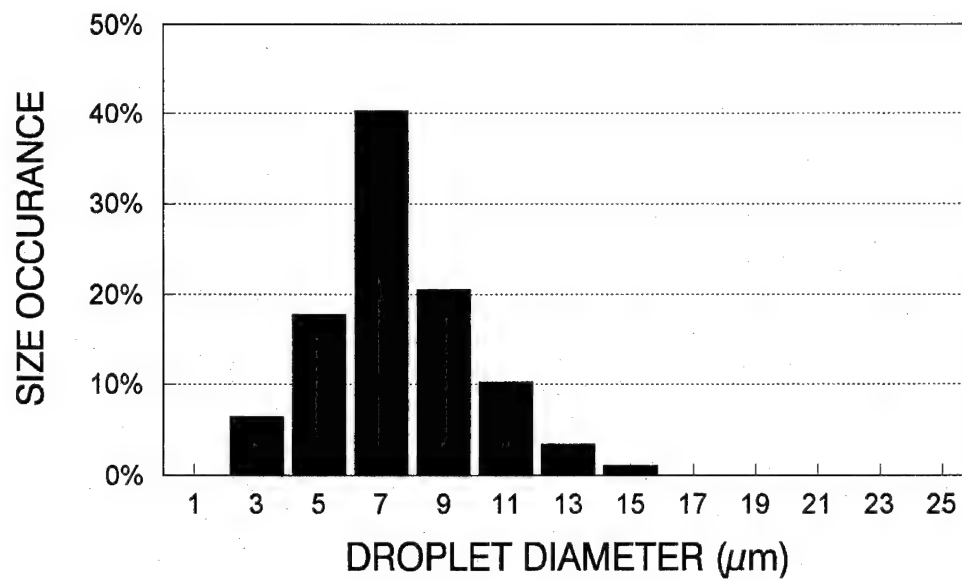


Figure 6. Example of typical droplet distribution where CALTECH and ASRC pH variations are within pH measurement error limits. Data averaged for 26 Jul 94, 1803-1903 UTC.

Acidity Dependence on Cloud Drop Sizes, Predicted Enhancement in Sulfate
Production in Clouds and its Climatic Implications

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ABSTRACT

Acidity variations between cloud droplets of different sizes are predicted in models, however, measurements made in natural clouds to verify this are extremely limited. The heterogeneity in cloud droplets may lead to increased sulfate production in clouds exceeding calculations made using bulk cloud water characteristics. During the spring, 1995, a size-fractionating version of the California Institute of Technology active strand cloud water collector was operated on a mountain-top platform in Mt. Mitchell State Park, North Carolina ($35^{\circ} 44' 05''$ N $82^{\circ} 17' 15''$ W) to determine, experimentally, whether acidity variations between large and small cloud droplets are common in nature as models suggest. Differences of up to 0.6 pH units were common for the sampled clouds with the small cloud droplets generally more acidic than the large droplets. We did collect several samples, however, where the large cloud droplets were more acidic. This chemical heterogeneity, though seemingly small, can significantly enhance oxidation of sulfur dioxide to sulfate within clouds, relative to oxidation rates predicted using bulk water samples. Our findings indicate that sulfate production rates, which could enhance cloud condensation nuclei, are underestimated by at least 5%, compared to bulk water calculations, for over 30% of our samples. These results suggest that sulfate production within clouds may be more rapid than previously theorized. In this study we not only examine cloud droplet chemical inhomogeneity between droplet sizes, but also examine the effect of air mass origin on those variations.

1. INTRODUCTION

Cloud water chemistry is significant because of its potential effect on the environment having both direct detrimental effects, such as adversely affecting forest growth through impaction (DeFelice and Saxena, 1991), and by altering cloud properties affecting the climate, such as albedo (Twomey, 1974, 1977, 1991; Charlson et al., 1992; Saxena et al., 1994). Atmospheric sulfate production is thought to play an important role in affecting cloud albedo. Atmospheric sulfates are believed to increase cloud albedo by increasing the cloud droplet number concentration. This tends to counteract the impact of increased greenhouse gases (Ghan et al., 1990; Charlson et al., 1991; Twomey, 1991; Lelieveld and Heintzenberg, 1992). A seemingly minor 2% change in the planetary albedo, in which cloud reflectance is a major contributor, would be roughly enough to offset climatic changes expected with a doubling of atmospheric CO₂ (Twomey, 1991). Low clouds, which also reside in that part of the atmosphere most subject to the influence of anthropogenic emissions, have very little effect on outgoing terrestrial longwave radiation since cloud temperatures are little different from the surface. However, reflectance of incoming shortwave radiation is not dependent on cloud height (Twomey, 1991). This suggests low clouds play a more important role in countering increased warming by greenhouse gases than high clouds.

Early models of acidic deposition assumed that all atmospheric sulfate production was the result of oxidation of SO₂ in the gas phase (Clark et al., 1989). Recently, however, several investigators (Hegg and Hobbs, 1981; McHenry and Dennis, 1991; Lelieveld and Heintzenberg, 1992; Easter and Peters, 1994) have come to believe the majority of global atmospheric sulfate production occurs in clouds. In the presence of oxidants such as ozone, hydrogen peroxide, or oxygen plus trace metal catalysts, sulfur dioxide can be oxidized more rapidly in the aqueous than in the gas phase (Seinfeld, 1986). To estimate possible climatic effects, such as increases in cloud droplet number concentrations leading to changes in cloud albedo, sulfate oxidation rates are often determined using bulk cloud water properties, such as cloud water pH (e.g. Hegg and Hobbs, 1981; Daum, 1990; DeFelice and Saxena, 1990b; McHenry and

Dennis, 1994), while models attempting to determine sulfate production rates often assume the aqueous-phase oxidation of SO_2 to sulfate is proportional to cloudiness (Langner et al., 1992). The "bulk water" approach not only assumes homogeneous chemical compositions between differing size cloud droplets, but also between cloud droplets of the same size. This view, in part, originated with the theory that in warm clouds, particularly stratocumulus, droplets become monodispersed over time (Wallace and Hobbs, 1977), and also based on analysis of cloud water collected from instruments with no means of fractionating droplet sizes. These single collections contained polydispersed drop sizes mixed together. While it is easy, and convenient, to obtain cloud water samples in this manner, the mixing of cloud droplets into bulk samples tends to mask chemical differences expected between droplets of different sizes (Ogren and Charlson, 1992). These variations in droplet size chemistry are important for understanding the climatic effects of clouds.

Ogren and Charlson (1992) have proposed a number of reasons for cloud drop populations to be chemically heterogeneous, based on the nature and type of the cloud condensation nuclei (CCN), varying droplet growth rates and varying rates of soluble gas uptake by different sized droplets. Models also predict large variations between large and small droplets both for acidity and chemical composition (Seidl, 1989; Twohy et al., 1989; Hegg and Larson, 1990; to name a few). This heterogeneity in cloud droplets may lead to increased sulfate production in clouds exceeding estimates made using bulk cloud water characteristics, especially for air originating in a marine environment (Hegg and Larson, 1990). If pH varies with cloud droplet size (Easter and Hobbs, 1974; Twohy et al., 1989), the sulfate concentration in cloud droplets also becomes size dependent (Hegg and Hobbs, 1979) thus affecting the droplet acidity. As demonstrated by Collett et al. (1994), when using bulk cloud water samples sulfate production rates can be seriously underpredicted for clouds where the acidity varies between large and small droplets, particularly where the small droplets are the most acidic. As shown by Yuen et al. (1994), this heterogeneity in chemistry across the cloud-droplet size distribution can have significant impact on in-cloud sulfate production. The underestimation on predicted in-cloud sulfate production increases as

the difference in the pH between different sized droplets increases (i.e. the smaller droplets become more acidic compared to the large). This enhancement is not limited, however, to samples where the smaller droplets are more acidic than the large. Only in cases where large and small droplet pH are approximately the same, will the bulk calculations for sulfate production be representative of the actual cloud.

The error in determining sulfate production rates in clouds based on bulk cloud water characteristics is important for two reasons. First, several investigators believe increased sulfate production generates a larger number of CCN upon which clouds can form (Radke and Hegg, 1972; Hegg, 1991; Langner et al., 1992; Lelieveld and Heintzenberg, 1992; Mitra et al., 1992; Leaitch and Issac, 1993; Easter and Peters, 1994), though there is no agreement on the generation mechanism. Given the same amount of water available for the cloud, this would produce a larger number of droplets with smaller average sizes (Saxena and Grovenstein, 1994b). This in turn is thought to affect the reflectivity of the cloud produced (Lacis and Hansen, 1974; Twomey, 1977; Kaufman and Fraser, 1991; Leaitch and Issac, 1993). As shown by Twomey (1991), not only do cloud cover changes affect climate, but surface temperatures can also be affected by changes in cloud reflectance without any changes in cloud amount. Secondly, increases in sulfate production increases atmospheric aerosols. This increase affects the scattering ability of the cloud-free air (Fleagle and Businger, 1963; Liou, 1980; Hinds, 1982; Charlson et al., 1991) and similarly acts to counter the effect of increased greenhouse gases. Figure 1 illustrates both the traditional and cloud-production views of sulfate production in the atmosphere and predicted effects of each on incoming solar radiation. In the cloud production view, the role of clouds in producing sulfates is enhanced. This is due to the effects sulfates produced in clouds have on the characteristics of subsequently formed clouds after the present cloud dissipates.

The argument, to this point, assumes that bulk cloud water samples are not representative of the cloud sampled, and variations in droplet acidity between small and large droplets will enhance sulfate production. Saxena et al. (1994) found clouds with smaller droplets and higher cloud droplet number concentrations are relatively more

acidic. This implies the smaller droplets were more acidic than larger droplets, while Burns et al. (1995) found cloud pH (from bulk water samples) is largely controlled by cloud droplet size and the cloud albedo is inversely proportional to cloud pH (i.e. more acidic clouds have many smaller droplets). It was not determined experimentally in either of these studies, however, whether the smaller droplets were indeed more acidic, only inferred from the "bulk water" sample and then related to measurements of cloud droplet number concentrations and droplet size distributions. Very limited studies (Munger et al., 1989; Collett et al., 1994) have been made to experimentally determine if cloud droplet compositions vary between drop sizes as theory predicts, and to ascertain whether this commonly occurs in nature.

In neither of the two previous studies which experimentally measured differences in variously sized cloud droplet pH was air mass origin taken into consideration to determine what effect, if any, cloud droplet composition was related to the origin of the air supplying the CCN from which the resulting clouds were formed. Cloud water pH variations have been found to be dependent on the origin of the cloud forming air mass (Saxena and Yeh, 1988; Saxena et al., 1989) so it is likely that variations in acidities between droplet size fractions are also air mass dependent. This is the first study we are aware of which not only examines cloud droplet chemical inhomogeneity between droplet sizes, but also examines the effect of air mass origin on those variations.

2. EXPERIMENTAL SITE AND INSTRUMENTATION

The experimental site for this study is located at Mt. Gibbs (2006 m MSL), approximately 2 km south of Mt. Mitchell, North Carolina. The site is ideal for *in situ* cloud measurements as the area is immersed in clouds nearly 70% of the time during the summer (Saxena et al., 1989, 1994), while being influenced by varying air mass types; highly polluted air from the Ohio Valley region, clean maritime air and relatively clean continental air from the great plains (Saxena and Yeh, 1988). Additionally, there is no local source of pollution near the experiment site allowing for the study of the long range transport of both natural and anthropogenic aerosol. Recently the site has been designated as a United Nations Biosphere Reserve so that our measurements, and those of others, can be used over a long period of time to accurately gauge regional climate change.

During the spring 1995, three cloud water collectors were operated simultaneously at a field station on Mt. Gibbs (elev. 2006m) in Mt. Mitchell (35° 44' 05" N 82° 17' 15"W - the highest peak in the eastern U.S) State Park, North Carolina. The collectors used were an Atmospheric Science Research Center, Albany, New York (ASRC) passive cloud water collector (Castillo et al., 1983; Saxena et al., 1989; DeFelice and Saxena, 1990a), a Daube California Institute of Technology active-string collector (CALTECH) (Daube et al., 1987) and a Size-Fractionating Caltech Active Strand Cloud water Collector (SFCASCC) as described by Demoz et al. (1995) mounted side-by-side on a rotating carriage at the top of an observation tower, above the forest canopy. The CALTECH and SFCASCC were operated with the precipitation shields removed (Logie and Saxena, 1995). Passive collectors depend upon ambient wind speed to provide the velocity differential between suspended cloud droplets and the collector surface, while active collectors provide some physical means (such as a fan) for generating the velocity difference. The SFCASCC collects two drop size fractions by impaction on Teflon rods and strands. The first bank, comprised of 10 rows of Teflon rods, has a 50% size cut to collect droplets of 23 μm in diameter and larger, while the second bank of the collector has a 50% lower size cut of 4 μm where

droplets are collected via impaction on 6 rows of Teflon strands. It should be noted that the size fractionating ability of the SFCASCC is not as sharp as would be found using a device such as a cascade impactor and some mixing between small and large droplets does occur (Collett et al., 1994). The period of observations for our study ran from early March intermittently through the middle of June covering 15 cloud events and 67 cloud samples from non-precipitating clouds.

An observation tower, 16.5 m tall extending roughly 10 m above the forest canopy, was instrumented with meteorological sensors for ambient temperature, relative humidity, barometric pressure and solar radiation. The liquid water content of the clouds (LWC) was determined using an RPM sampler, designed by the Tennessee Valley Authority (Valente et al., 1989) and from an empirical relationship between collected cloud water and LWC utilizing the ASRC cloud water collector (Saxena et al., 1989; DeFelice and Saxena, 1990a).

The cloud water collectors used in this experiment were manually operated on an hourly basis upon the occurrence of a cloud event. A cloud event began when a stationary object at a distance of 1 km from the tower became immersed in clouds and stayed consistently obscured from view for a period of at least 15 minutes. The stationary object was conveniently chosen as a television tower which also had an unfocused red light on it facilitating nocturnal observations. The cloud water collected was tested for pH within minutes of collection using two samples, if sufficient quantity had been collected, with the remaining sample refrigerated at 4 C for future chemical analysis using a Dionex 2010i ion chromatograph. The chemical composition of the collected cloud water was analyzed with conventional USA EPA QA/QC procedures by the Soil Sciences Lab at North Carolina State University. Additionally, for several of the cloud events, the final cloud water sample was followed by a control sample of deionized water to help validate lab analysis results.

Limited Forward Scattering Spectrometer Probe (FSSP) (Knollenberg, 1981) data were available near the end of this study. The FSSP was deployed on the same movable carriage as the ASRC and SFCASCC. The CALTECH non-fractionating collector was removed to allow mounting of the FSSP during this portion of the study.

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The FSSP was used to obtain cloud droplet number concentrations and size distributions of cloud particles over specific time periods. During a cloud event the FSSP would be activated and pointed into the wind. The cloud microphysical parameters were then instantly transmitted to a desktop computer where they were saved for subsequent data reduction.

Air mass trajectories for all cloud events were calculated using the Hybrid Single-Particle Lagrangian Integrated Trajectories (HY-SPLIT) Model (Version 3.0) developed at the National Oceanic and Atmospheric Administration (Draxler, 1992, Mueller, 1994).

3. RESULTS AND DISCUSSION

Sulfate Production Rates in Clouds.

Sulfate production rates in clouds are often determined using the pH of bulk cloud water samples (e.g. Hegg and Hobbs, 1981; Daum, 1990; DeFelice and Saxena, 1990b; McHenry and Dennis, 1994). This practice assumes sulfate production rates based on integrated samples are the same for both the small and large cloud droplets, and the cloud water possesses a uniform chemical composition. Models, however, predict a substantial variation in cloud drop composition between droplet sizes, and this heterogeneity increases sulfate production within clouds (e.g. Seidl, 1989; Twohy et al., 1989; Hegg and Larson, 1990). Seinfeld (1986) showed that although sulfur dioxide oxidation by hydrogen peroxide is largely independent of acidity over the pH range observed in cloud water, oxidation by ozone, and by oxygen catalyzed by Fe(III) or Mn(III), is not. Considering Hegg and Larson's (1990) results as an example, calculated in-cloud SO_4^{2-} production was found to be anywhere from 3 to 30 times higher than in a bulk model when explicit drop size microphysics was included. Utilizing the same procedure used by Hegg and Hobbs (1979) and Hegg and Larson (1990), and drawing on Seinfeld (1986), we have determined how sulfate production rates vary as the acidity between cloud droplet fractions increases for the oxidation of sulfur dioxide by ozone. A functional relationship for the oxidation of sulfur can be expressed as:

$$\frac{d(SO_2)}{dt} = 0.043835 \exp[2.186pH]. \quad (1)$$

Differing contributions of acids and bases to individual cloud drops produce a distribution of drop acidities. Figure 2 compares the pH values of small and large cloud drops for 63 non-precipitation sample pairs collected at Mt. Mitchell. The range of pH values observed, from less than 3 to nearly 5 depicts a varying range of cloud compositions included. Our measurements show a wider range of pH variation than Collett et al. (1994) found in their cloud water collections at Mt. Mitchell, probably due to both the different time of the year we made our collections, and because we

collected significantly more samples than they did. However, similar to their study, we did not find pH variations between drop fractions greater than 0.6 pH units. While in the majority of cases the small droplets were more acidic than the large, there were also some exceptions. While differences in pH as large as 2 units have been observed between large and small drop fractions collected with the SFCASCC, pH differences have generally been found to be less than one unit (Demoz et al., 1995) as we found in our sample collections.

Let us first examine how sulfate production rates can be affected in a hypothetical cloud where 30% of the cloud's liquid water content is in small drops of pH 4 and the remaining portion is in the large droplets. As the drop pH for the large droplets is varied from 4 to 5 (the pH difference between the fractions increases from 0.0 to 1.0 pH units), the sulfate production rate increases from $275 \mu\text{mol l}^{-1} \text{min}^{-1}$ to $2447 \mu\text{mol l}^{-1} \text{min}^{-1}$ (eq. 1). This represents an enhancement by a factor of 8.9 (Fig 3).

We will now examine how sulfate production rates are predicted for clouds encountered at our site. We will consider two cases where the pH differs between the large and small droplet fractions. The LWCs for the drop fractions was determined by the ratio of collected water for each stage of the SFCASCC to the total collected by the device (Collett, J. L. Jr., personal communication, 1995). The average cloud water pH was determined by using the computed LWC for each fractionated sample and the hydrogen ion concentrations. By doing this the absence of weak acids and bases was assumed. Conservative mixing of H^+ is an oversimplification when weak bases and acids are present (Perdue and Beck, 1988). While we did collect bulk water samples using an ASRC and a CALTECH collector, we did not use the measured pH from those devices as representative of our average pH due to the different collection efficiencies between the fractionating and non-fractionating collectors (Castillo et al., 1983; Daube et al., 1987; Collett et al., 1994) though we had planned to. For example, in cases where the small droplet pH was more acidic than the large droplet pH, the improved collection efficiency of the ASRC and CALTECH collectors to capture small droplets (size cutoff approximately $0.5 \mu\text{m}$ lower than the SFCASCC) resulted in bulk water samples with pH values nearer the droplet pH for the small droplets. For

samples where the small droplets were less acidic than the large droplets, the opposite result was true. While using these bulk measurements would serve to enhance the results that follow, we would not be making a directly applicable comparison to our SFCASCC samples so we chose to use the calculated average cloud water pH instead.

The first case uses cloud water obtained on May 27, 1995 (1230-1330 UTC). The average cloud water pH of the sample is 4.39 and the cloud liquid water content is 0.219 g m^{-3} . Figure 4 illustrates a typical sample composition for this type of case where the small droplets are more acidic than the large. From our fractionated cloud water sample, we find 28 percent of the cloud LWC is comprised of small droplets with a pH of 4.14 while the remaining LWC consists of large droplets with a pH of 4.51. For the bulk water sample, the sulfate production rate is predicted to be $645 \text{ } \mu\text{mol l}^{-1} \text{ min}^{-1}$. Now if we determine sulfate production rate based on our fractionated sample, the predicted rate increases to $708 \text{ } \mu\text{mol l}^{-1} \text{ min}^{-1}$. This represents an enhancement of about 10% (or a 10% underprediction using the bulk water pH).

The second case utilizes cloud water obtained on March 5, 1995 (1630-1730 UTC). The average pH of the cloud sample is 4.10 and the cloud liquid water content is 0.381 g m^{-3} . Figure 5 illustrates a typical sample composition for this type of case where the large droplets are more acidic than the small. From our fractionated cloud water sample, we now find that 16 percent of the cloud LWC is comprised of small droplets with a pH of 4.56 while the remaining LWC consists of large droplets with a pH of 4.05. For the bulk water sample, the sulfate production rate is now predicted to be $342 \text{ } \mu\text{mol l}^{-1} \text{ min}^{-1}$. Again, if we determine sulfate production rates based on our fractionated sample, we find the sulfate production rate is still underestimated, and the new rate is $407 \text{ } \mu\text{mol l}^{-1} \text{ min}^{-1}$. This case illustrates how even in samples where the large droplets are more acidic than the small droplets, large differences in pH between the small and large drop size fractions and the average cloud water pH can still lead to underprediction of sulfate production. In this case sulfate production is underpredicted by about 20%.

Figure 6 depicts the calculated enhancement in sulfur oxidation by ozone as a result of the chemical heterogeneity within the cloud for all samples. The data is

presented as a frequency distribution of samples with various oxidation rate enhancements. The average rate of sulfur oxidation in a cloud with two distinct drop compositions was divided by the oxidation rate predicted using the average cloud drop composition for each pair of large and small drop fractions. Approximately 68% of the samples were determined to experience less than 5% enhancement in the oxidation rate. Another 25% of the samples were calculated to experience between 5% and 19% enhancement in the oxidation rate, while the remaining 7% were expected to experience over 20% enhancement. The largest enhancement calculated was 28%.

While in nature we do not expect real clouds to contain only two chemically distinct drop populations, nor is it likely that all drops of the same size will have the same acidity, so similar to bulk water determinations of sulfate production rates, the estimates made here are probably more conservative than actually occurs in clouds. A wider distribution of drop compositions will magnify the results of this study so that even faster sulfur oxidation rates can be realized if cloud water samples can be obtained with either a sampler with a sharper size cutoff than available from the SFCASCC, or by using a device which will fractionate the droplets into more than two size ranges.

Influence of Air Mass Trajectory on Large and Small Cloud Droplet Chemistry.

1) Cloud droplet pH:

We have seen how cloud droplets can have varying acidities between large and small droplet size fractions. What we would like to determine now is whether particular variations in pH (i.e. smaller droplets always more acidic than large) are common to any specific air mass origin(s). This may be useful in determining whether we can easily identify situations likely to exhibit sulfate production rates greater than predicted using bulk cloud water measurements. This could also enable us to review previous sulfate production predictions based on bulk cloud water properties and, after determining the origin of the air creating a particular cloud, be able to infer with some confidence, whether the predicted sulfate production rate was actually representative of the cloud or not. We must realize though that this is still only an estimate.

Figure 7 relates droplet pH variations between small and large droplets to backward trajectories indicating the air mass origin as marine, continental and continental/marine. A mixed air mass origin (i.e. continental/marine) indicates that the 48 hr backward trajectory for a particular cloud event crossed from one regime to another. Three sectors, identified as the polluted sector, from 290° to 65° azimuth relative to the site, the continental sector, 240° to 290° azimuth, and the marine sector, 65° to 240° azimuth, were used to classify the cloud forming air masses. Characterization of air masses traversing the Mount Mitchell observation site was accomplished by utilizing anthropogenic emissions data of SO_x and NO_x available from the U.S. Environmental Protection Agency (EPA, 1993). Two important results immediately stand out. First, for the marine air mass cases, the pH of the smaller droplets are more acidic than the large droplets over 80% of the time, and never less acidic. We also found a mixed polluted/marine air mass (not shown) produced samples where the small drop pH was always more acidic than the large. We did not include the latter results, however, since we only collected 6 samples during a single cloud event. From the previous discussion this would tend to imply that sulfate production rates for clouds originating from marine air masses are generally underpredicted using bulk cloud data at Mt. Mitchell. This agrees with predictions concerning sulfate production in clouds formed by air originating in a marine environment made by Hegg and Larson (1990). The second notable fact is that for air masses originating in the continental regime, including a mixed continental/marine regime, there is no predictable relationship between acidity and droplet size so no case can be made for past sulfate production rate inaccuracies without actual fractionated cloud droplet measurements. However, continental air masses do yield larger differences in the large and small drop pH values, particularly in the more acidic clouds.

2) *Sulfate concentrations*

Concentrations of sulfate in large and small drop fractions collected at Mt. Mitchell are shown in Figure 8. Small drops generally contained higher sulfate concentrations than the large droplets; occasionally much higher. By using a

fractionating collector, we found it was also not uncommon (nearly 20% of the samples) for the larger droplets to have higher sulfate concentrations than the small droplets. Additionally, as illustrated in Figure 9, SO_4^{2-} concentrations are negatively correlated with pH of the small cloud droplets with a correlation coefficient of -0.74. This is in general agreement with the findings of Saxena and Lin (1990) and Burns et al. (1994) that lower cloud water pH corresponded to higher sulfate concentrations, increased cloud droplet number concentrations and smaller average droplets. A plot of SO_4^{2-} against pH for the large droplets did not show a significant correlation, however.

Climatic Implications for Increased Sulfate Production in Clouds.

We have seen how sulfate production rates can be underestimated in clouds using bulk (average) cloud properties where the larger droplets are less acidic than the smaller droplets, and in some cases where the smaller droplets are less acidic, and that the underprediction increases as the acidity variation increases between the drop size fractions. It is not clear, however, what effect, if any, this underprediction may have on previously estimated climate changes.

There are three basic hypotheses concerning the effect increased sulfate production has on clouds which are still being debated. One theory predicts increased sulfate production will lead to more particles upon which cloud droplets can form, thereby increasing the cloud droplet number concentration (Hegg, 1991; Lelieveld and Heintzenberg, 1992; Leaitch and Issac, 1993; Easter and Peters, 1994).. This would result in increased numbers of CCN upon which subsequent clouds could form once the present cloud is dissipated, but not increase the CCN concentration cloud where sulfate production is occurring. A second theory holds that increased sulfate production will not lead to more particles, but will increase the size of existing particles (Langner et al., 1992). In addition to growing larger droplets, this would allow more particles to become activated at a given supersaturation. This would also tend to increase cloud droplet number concentration as more particles are activated and able to form cloud droplets. Finally, a third theory suggests that, similar to the previous theory, increased sulfate production would lead to larger, not more, sulfate particles in the cloud, but

would tend to break up into smaller particles during the cloud dissipation process (Radke and Hegg, 1972; Mitra et al., 1992). While all three theories predict different consequences for increased sulfate production in clouds, they all have the same end result: increased CCN upon which subsequent clouds could form implying larger cloud droplet number concentrations given no change in available water vapor. As Saxena and Grovenstein (1994a) found in their study, elevated CCN concentrations occurred within, and near, stratus clouds sampled in Alaska. They concluded that clouds act not only as a sink of CCN, but also as a source.

Ghan et al. (1990), Charlson et al. (1991), Twomey (1991), and Lelieveld and Heintzenberg (1992) hypothesized that atmospheric sulfate production increases cloud albedo by increasing the cloud droplet number concentration. Kaufman and Fraser (1991) and Leaitich and Issac (1993) believe this increase in sulfate aerosol available as CCN acts to increase the cloud droplet number concentration (CDNC) by the following:

$$\frac{\Delta N_d}{N_{d0}} = \frac{2.23 \Delta m_{SO_4}}{N_{c0}} \quad (2)$$

where ΔN_d is the increase in CDNC, N_{d0} is the CDNC before anthropogenic influence, Δm_{SO_4} is the increase in the mass of sulfate in the aerosol, and N_{c0} is the CCN concentration before anthropogenic influence. This in turn could act to counter the effect of increases in greenhouse gases through increased scattering and reflection of incoming solar radiation, thus acting as a cooling mechanism. As an example of this effect consider a hypothetical cloud with a depth of 100 m. The optical depth, τ , is related to the number of cloud droplets, N_c , the liquid water content, LWC, the cloud thickness, h , and the density of liquid water, ρ_w by the relationship (Twomey et al., 1984):

$$\tau = h \left[\frac{9\pi (LWC)^2 N_c}{2\rho_w^2} \right]^{1/3} \quad (3)$$

From Lacis and Hansen (1974) the albedo of the cloud, A_c , can now be evaluated in terms of the optical depth as

$$A_c = \frac{\tau}{7.7 + \tau}. \quad (4)$$

Together these three equations show how, as the cloud droplet number concentration is increased due to atmospheric sulfate production, with no change in available cloud liquid water, the albedo of the cloud increases. Figure 10 illustrates how cloud albedo can change for various cloud droplet number concentrations for three different cloud liquid water contents. From the diagram it is apparent that the rate of increase in cloud albedo is greatest when droplet number concentrations are relatively small; the range typically associated with cleaner marine clouds. This is the same type of air mass in which smaller cloud droplets are generally more acidic than large droplets (Fig. 7). This infers that sulfate production rates predicted using bulk cloud water measurements will generally be lower than expected to occur in the actual clouds formed from air originating in a marine environment. From theory, increased sulfate production leads to increased CCN, hence increased cloud droplet number concentrations in subsequently formed clouds, and therefore higher cloud albedo. While this is mostly theoretical at this point, at least locally, this could tend to counter any expected warming caused by greenhouse gases. Recall that in over 30% of the samples collected during this study, sulfur oxidation enhancement rates exceeded 5%. While these results suggest a local counter-balancing element to greenhouse warming caused by increases in CO₂, there is no evidence that this result can be applied globally.

Recall, however, that in nearly 20% of our samples the large cloud droplets had higher sulfate concentrations than the small droplets. This indicates that the larger droplets must have nucleated on the largest CCN (Noone et al., 1988; Heintzenberg et al., 1989; Ogren et al., 1992; Demoz et al., 1994). According to Albrecht (1989) it is these larger droplets that will be the first to grow large enough to drizzle out in stratus or stratocumulus clouds. This will tend to decrease the sulfate available for future cloud formation, since it is being precipitated out of the cloud, rather than acting to increase CDNC by increasing CCN. Considering this effect on eq. (2), with no other influences, the result is a net decrease in available cloud condensation nuclei. Applying this result to eqs. (3) and (4) thereby yields a decrease in cloud optical depth and

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subsequently cloud albedo. This does not then produce the cooling effect expected due to increased sulfate production within clouds as has been assumed up to this point.

4. CONCLUSIONS

Sulfate production in clouds is a critical component of the global sulfur cycle. It has been found that clouds with high sulfate concentrations generally have lower average acidities, smaller average droplet sizes and larger cloud droplet number concentrations than clouds with lower sulfate concentrations (Saxena et al., 1994). Several investigators (Hegg and Hobbs, 1981; McHenry and Dennis, 1991; Lelieveld and Heintzenberg, 1992; Easter and Peters, 1994) have come to believe the majority of global atmospheric sulfate production occurs in clouds. In the presence of oxidants such as ozone, hydrogen peroxide, or oxygen plus trace metal catalysts, sulfur dioxide can be oxidized more rapidly in the aqueous phase (Seinfeld, 1986). Traditionally, bulk water measurements of cloud water acidity have been used to estimate sulfate production within clouds. While it is easy and convenient to use bulk water measurements to infer in-cloud sulfate production rates, it tends to mask chemical differences between droplets of different sizes, and also between droplets of the same size. Both models, and limited measurements from natural clouds, suggest that cloud drop populations are chemically heterogeneous. Measurements of pH variations between large and small cloud droplets within natural clouds taken at Mt. Mitchell State Park, NC, reveal that small droplets are often, but not always, more acidic than large droplets. This chemical heterogeneity between small and large droplets can significantly enhance oxidation of sulfur dioxide to sulfate within clouds relative to production rates determined using bulk cloud water samples. Increased sulfate production in clouds is also important for its effect on regional climate. As clouds form and dissipate, it is theorized that increased sulfate production leads to increased cloud condensation nuclei (CCN) on which new clouds can form (Radke and Hegg, 1972; Hegg, 1991; Langner et al., 1992; Mitra et al., 1992; Leaitch and Issac, 1993; Easter and Peters, 1994), though how this creation of new CCN occurs is still under debate. With no change in available liquid water, the increased CCN leads to smaller droplets and larger number concentrations. Our results indicate that sulfate production rates, which could enhance CCN, are underestimated by at least 5%, compared to bulk water

calculations, for over 30% of our samples, with a maximum underprediction of 28%. Since increases in cloud droplet number concentration are thought to be directly related to cloud albedo (Saxena and Grovenstein, 1994b), it is expected that increases in CCN will increase cloud albedo, thus acting, at least regionally, to cool the Earth. In nearly 20% of our samples, however, we found that the large droplets had higher sulfate concentrations than the small droplets. This indicates that the larger droplets must have nucleated on the largest CCN (Noone et al., 1988; Heintzenberg et al., 1989; Ogren et al., 1992; Demoz et al., 1994). Since these larger droplets will be the first to grow to a size large enough to drizzle out of the cloud (Albrecht, 1989) the effect will be a decrease, rather than an increase in sulfate available for future cloud formation. Considering this effect on the theoretical equations for changes in cloud droplet number concentration, cloud optical depth and cloud albedo, there is no subsequent cooling since there will be no CCN increase for subsequent clouds, hence no countering effect to increased greenhouse gases.

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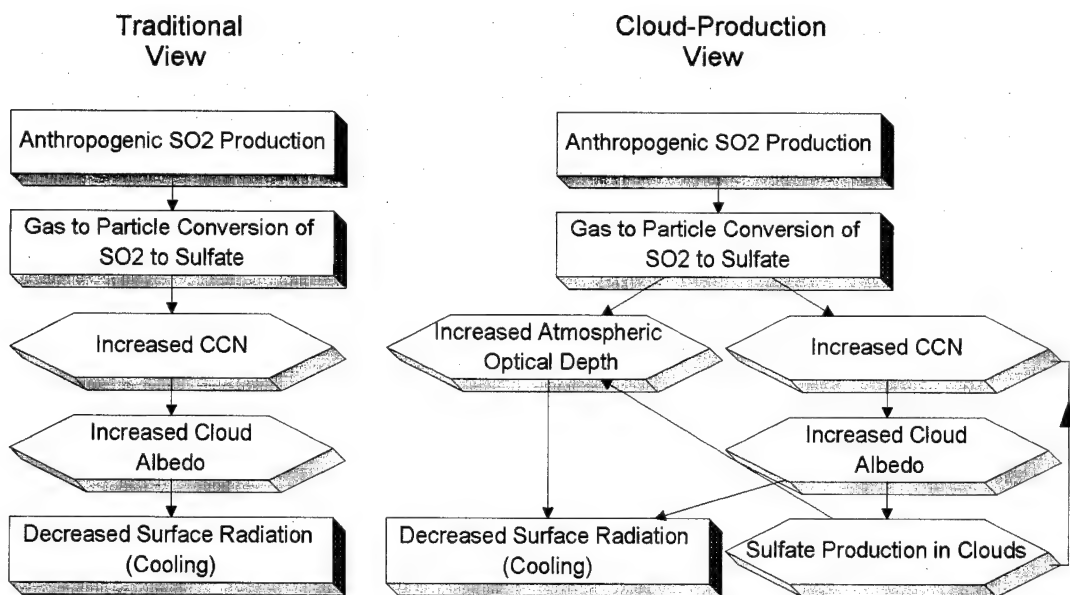


Figure 1. Diagram of the traditional and cloud-production views of sulfate production in the atmosphere and expected climatic effects.

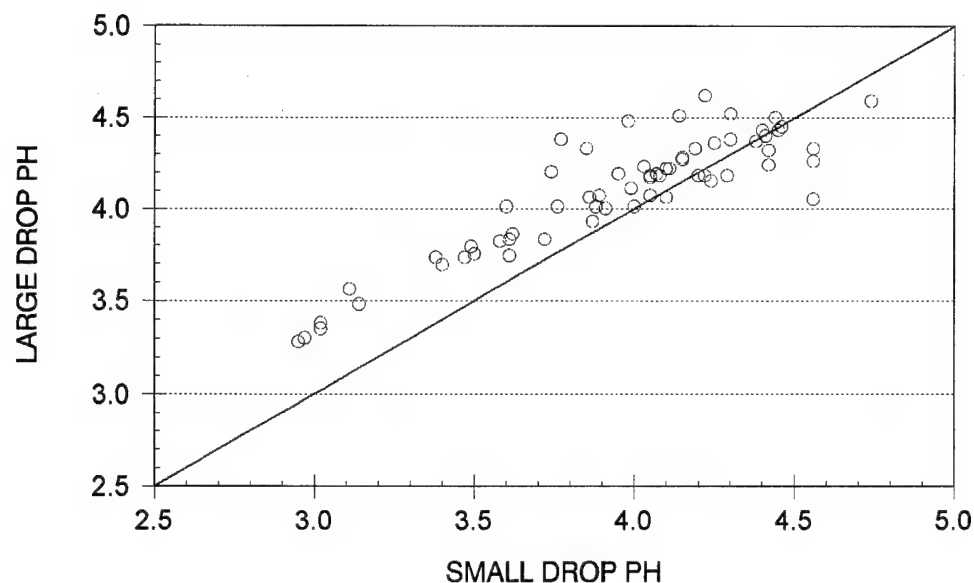


Figure 2. Small and large droplet fraction pH for collected cloud water samples. Small drop samples include cloud drops between 4 and 23 μm in diameter. Large drop samples include drops larger than 23 μm in diameter. The samples selected are from non-precipitating clouds with pH values ranging from 2.9 to 4.7. The solid line represents the one-to-one line where the pH from both size fractions is the same.

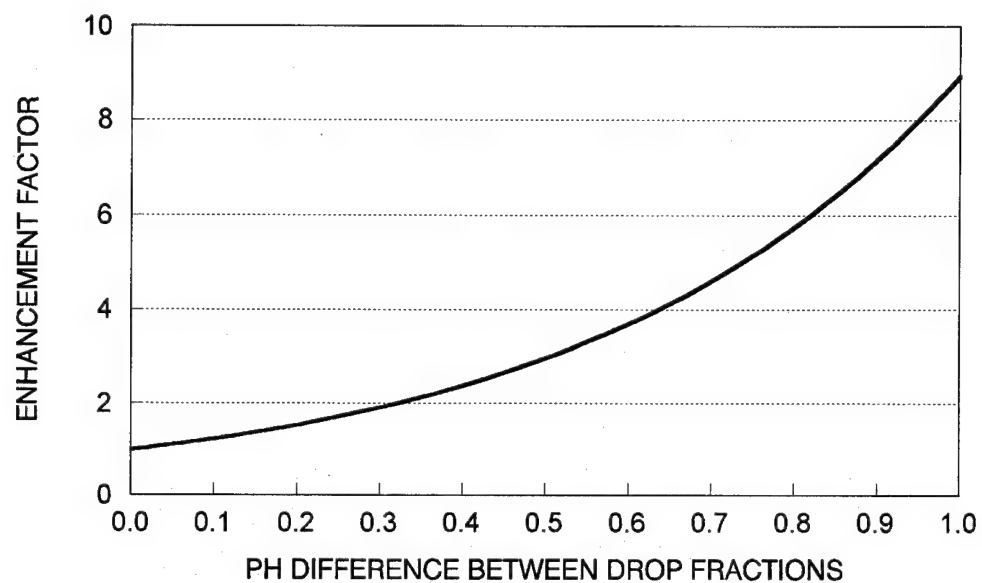


Figure 3. Variation of sulfur oxidation rate enhancement factor as a function of pH difference between large and small drop fractions.

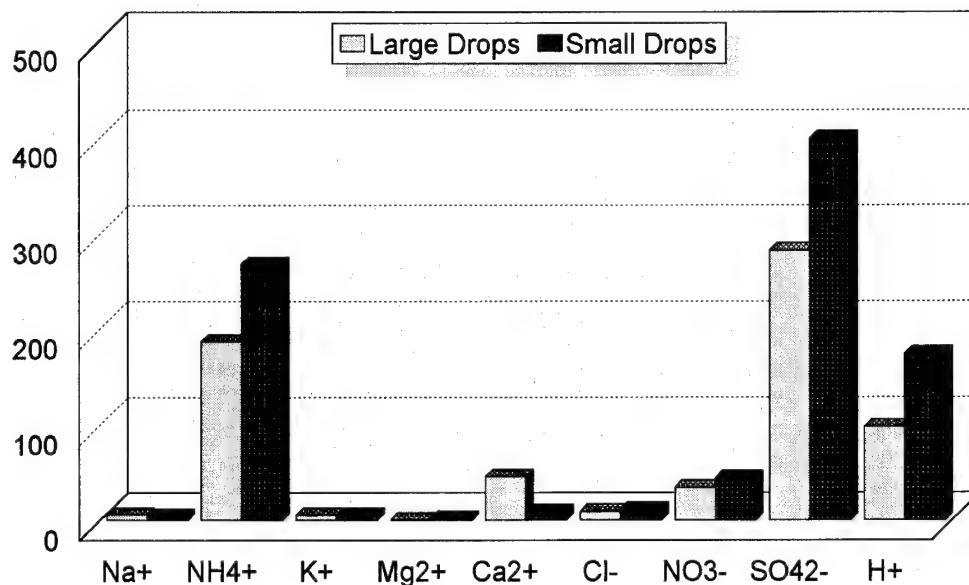


Figure 4. Concentration of major ions in small and large drop fractions collected on April 4, 1995 from 1800 to 1900 UTC. NH_4^+ , NO_3^- , SO_4^{2-} and H^+ concentrations are higher in the small drop fraction (diameters between 4 and 23 μm), while concentrations of Ca^{2+} are higher in the large drop fraction (diameters larger than 23 μm). The concentrations of Na^+ , K^+ , Mg^{2+} and Cl^- are nearly identical for both drop size fractions and only in trace amounts.

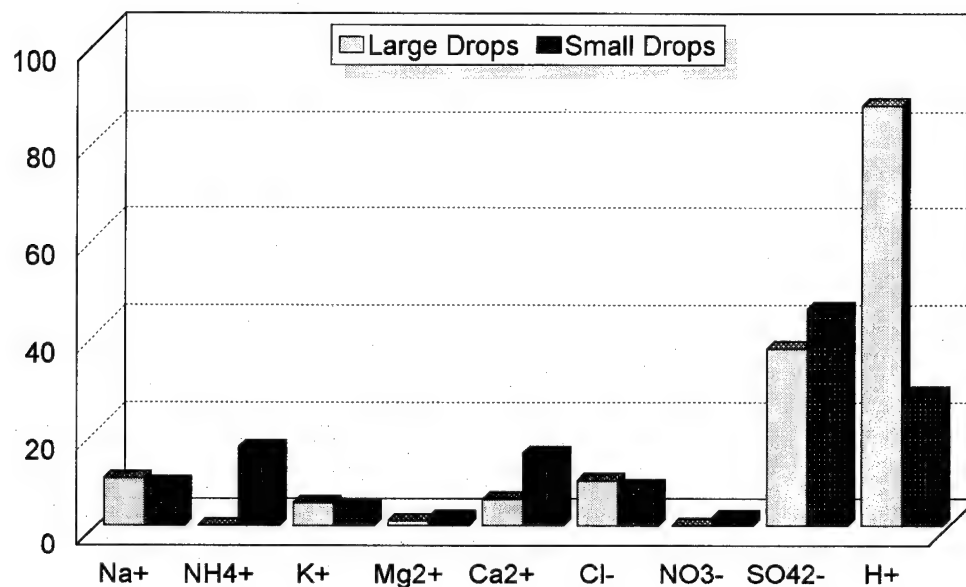


Figure 5. Concentration of major ions in small and large drop fractions collected on March 5, 1995 from 1530 to 1630 UTC. NH_4^+ , Ca^{2+} , and SO_4^{2-} concentrations are higher in the small drop fraction (diameters between 4 and 23 μm), while concentrations of H^+ are higher in the large drop fraction (diameters larger than 23 μm). The concentrations of Na^+ , K^+ , Mg^{2+} , Cl^- and NO_3^- are nearly identical for both drop size fractions and only in trace amounts.

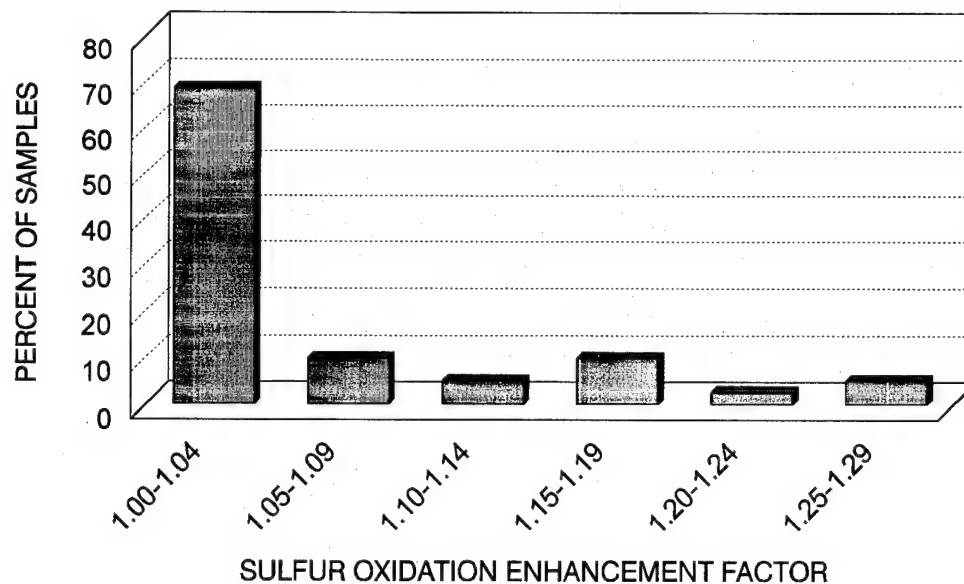


Figure 6. Calculated enhancement of sulfur oxidation by ozone due to chemical heterogeneity between small and large drop fractions within a cloud. The data is presented as a frequency distribution of samples with various ranges of oxidation rate enhancement. The average rate of sulfur oxidation in a cloud with two distinct drop compositions was divided by the oxidation rate predicted using the average cloud drop composition.

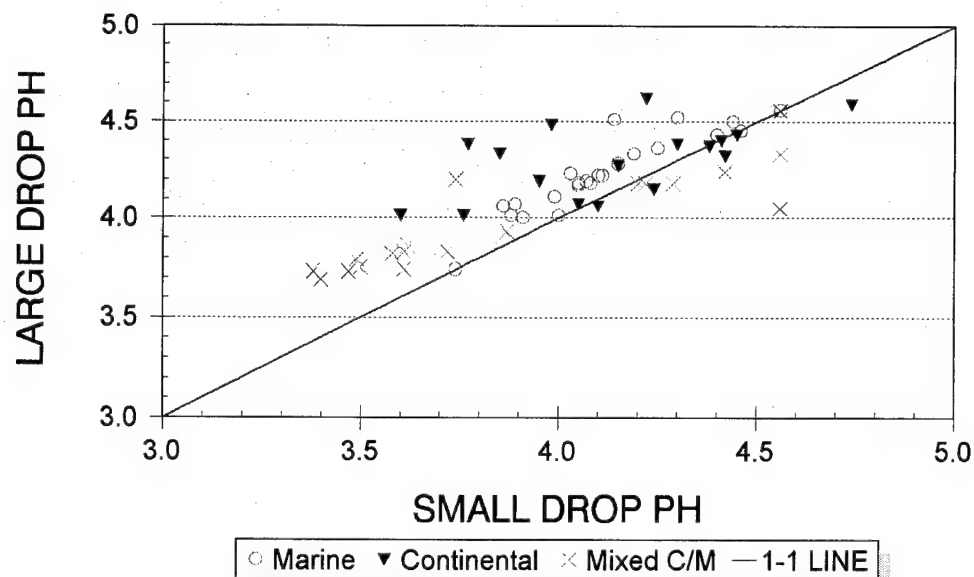


Figure 7. Small and large droplet fraction pH for collected cloud water samples with air masses originating in a marine, continental or mixed continental/marine environment. Small drop samples include cloud drops between 4 and 23 μm in diameter. Large drop samples include drops larger than 23 μm in diameter. The samples selected are from non-precipitating clouds with pH values ranging from 3.69 to 4.62. The solid line represents the one-to-one line where the pH from both size fractions is the same.

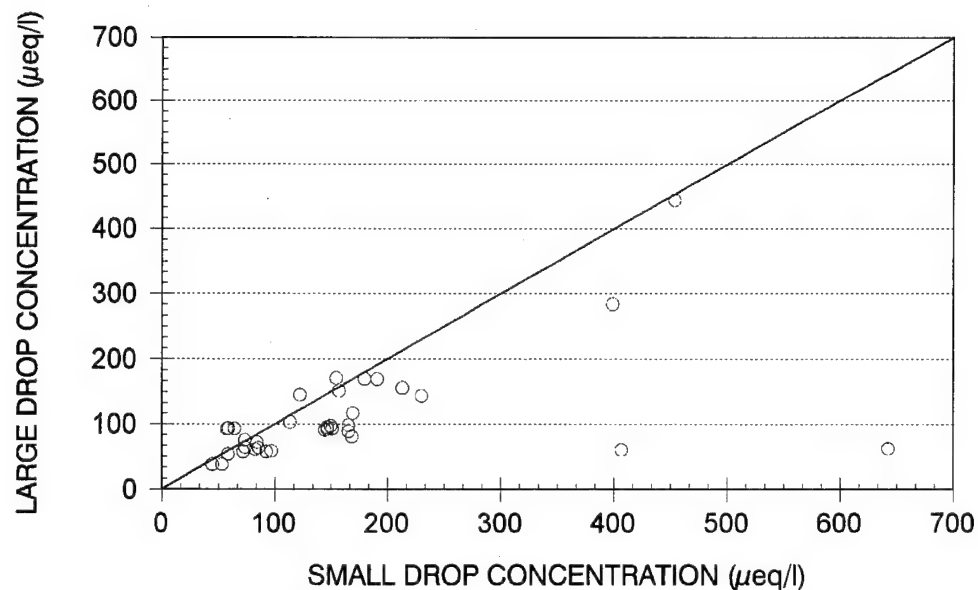


Figure 8. Sulfate concentrations in large and small cloud drop fractions collected at Mt. Mitchell, NC. Samples were collected with a Size Fractionating Caltech Active Strand Cloud water Collector. Small drop samples include cloud drops between 4 and 23 μm in diameter. Large drop samples include drops larger than 23 μm in diameter. The samples selected are from non-precipitating clouds with pH values ranging from 2.9 to 4.74. The solid line represents the one-to-one line where the sulfate concentration from both size fractions is the same.

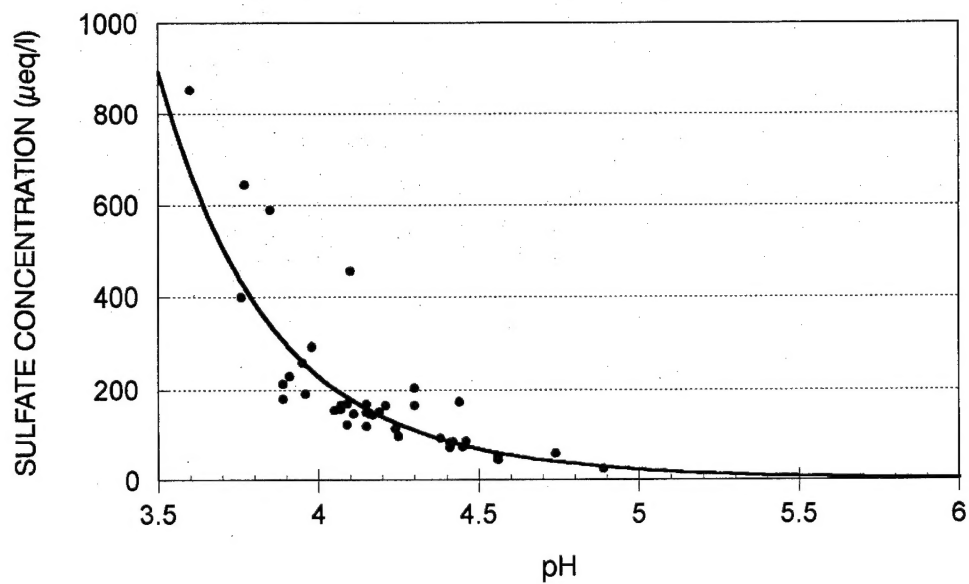


Figure 9. Scattering plot for sulfate vs. pH of small droplets. The curve represents the best fit line to the data using a power regression equation.

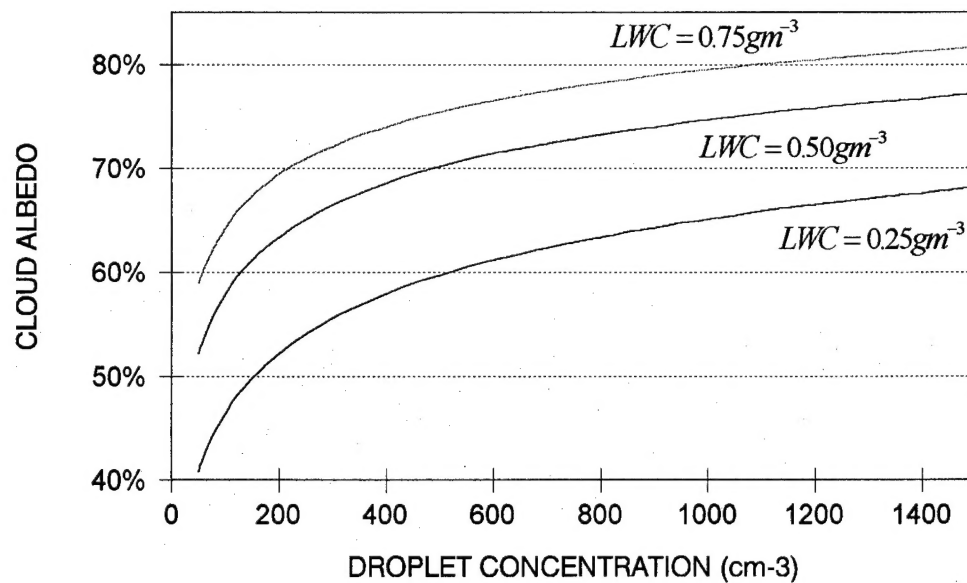
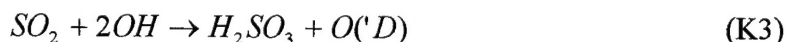


Figure 10. Cloud albedo as a function of droplet concentration under various cloud liquid water contents (LWC) for a hypothetical cloud 100 m thick.

APPENDIX

DETERMINATION OF SULFATE PRODUCTION BY SO₂ OXIDATION BY OZONE

Sulfur dioxide oxidation is the most rapid in the condensed phase, particularly in water drops (Seinfeld, 1986). The SO₂ is transported close to the cloud droplet by large scale, then small scale transport (read turbulence and molecular diffusion) processes.



combine to produce a non-linear equation:

$$\frac{d(SO_2)}{dt} = -\frac{K1 * K2 * K3}{K4} [H^+]^2 \quad (1)$$

From this relationship, an equation for the oxidation of sulfur in clouds by ozone can be expressed as (Hegg and Larson, 1990):

$$\frac{d(SO_2)}{dt} = 0.043835 \exp[2.186 pH]. \quad (2)$$

The following chemical assumptions were made to arrive at eq. (2):

- Maximum surface radiation (high noon on summer solstice with no clouds)
- Temperature = 25 C
- [SO₂] = 100 p.p.t.v. and does not diminish with time
- [O₃] = 25 p.p.t.v. and does not diminish with time
- Total molecular diffusion across air/water surface
- Gases are in equilibrium with liquid species
- No other species considered in the model (ammonia, etc.)

- Cloud LWC = 0.30 gm^{-3}
- Average cloud droplet radius = $4 \text{ }\mu\text{m}$ with a Kirhigan-Mazin droplet size distribution.